

Synthesis, Photochemistry and Photophysical Properties of Cyclooctene and Cyclooctenone Derivatives

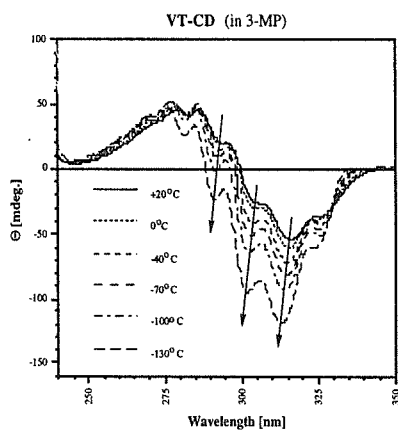
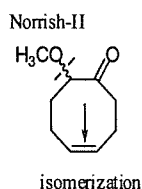
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シクロオクテン及びシクロオクテノン誘導体の 合成と光化学、光物理的性質

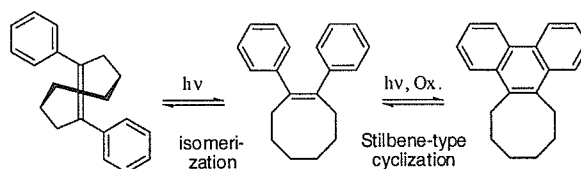
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Cyclooctene derivatives are known to undergo clean photochemical *Z-E* isomerization upon direct and sensitized excitation. Additionally, they are also very promising compounds for absolute asymmetric synthesis (AAS) using circular polarized light (CPL). The incorporation of other functional groups along the cyclooctene skeleton can lead to drastically changes in the photochemistry, and can open competing photo-processes. *E.g.*, whereas 4-cyclooctenone still undergoes clean photoisomerization, the branched (*Z*)-8-methoxy-4-cyclooctenone shows fragmentation due to Norrish-II reactions. On the other hand, enantiomerically pure (*Z*)-8-methoxy-4-cyclooctenone shows a very unique UV-CD behavior, and we have used several techniques, such as various temperature VT-CD (Figure), UV-Vis, NMR, Raman and IR, in order to investigate this unusual phenomenon.



Furthermore, the photochemistry of diphenylcyclooctene has been examined. Since this compound carries a stilbene fragment, it undergoes competing photocyclization to the corresponding dihydrophenanthrene derivative. Further oxidation in the presence of traces of oxygen yields its phenanthrene derivative.



As an example of a multichromophoric compound, we have succeeded in the synthesis and characterization of a new chiral *spiro*-linked cyclooctenone dimer. On irradiation, this compound was expected to undergo several competing processes.

